Manuscript: “Remote sensing of volcanic CO_2, HF, HCl, SO_2, and BrO in the downwind plume of Mt. Etna” by A. Butz et al.

Reply to comment by anonymous referee #1 (all page and line number refer to the AMTD version of the manuscript).

We thank the referee for the comments on our manuscript. Please find our point-by-point reply below.

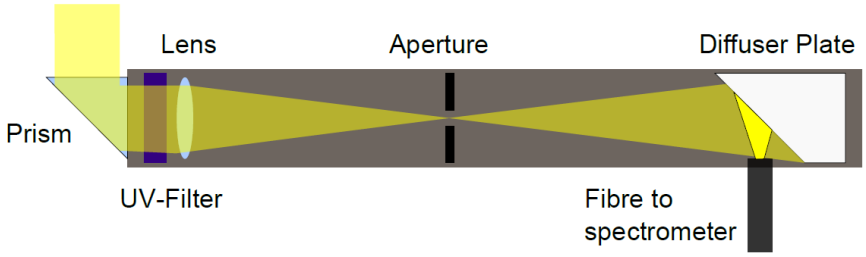
<<This is a well written paper about the measurement of the volcanic gas composition of Mt Etna’s with mobile remote sensing instrumentation. Although the concepts are not new since similar investigations have already been performed around the world, the authors do an excellent job describing the experimental and analytical techniques employed. Furthermore, the advances made recently in the improvement of commercially available instrumentation (i.e. robust spectrometers, refined solar tracking systems) was taken advantage of in order to get unprecedented precision in the detection of gases like CO_2 from the volcanic plume via the solar absorption technique. Much is still to be improved, as the authors comment, but this manuscript provides a very good insight of what is possible in terms of quality of the results with the now available technology. The article should be published in AMT after the following recommendations are taken into consideration.>>

<<- Give more detail on the optical set-up of the UV spectrometer/telescope in p4 l4 and provide a reference if available.>>

We add some text on the UV spectrometer:

> *Page 4:*
> *The UV grating spectrometer is an AvaSpec-ULS2048x64-ENV5 manufactured by Avantes. It features a 1,800 lines/mm grating and 2048 pixel linear array CCD detector covering the spectral range 294 to 457 nm. The entrance slit of the spectrometer is 200 μm wide supporting an optical resolution of 0.8 nm (FWHM). The spectrometer is placed inside a housekeeping box (EnviMesS TSE 1.1) equipped with a Peltier cooling that keeps the spectrometer temperature stable at 15.00°C with a precision of 0.02°C. The housekeeping box disposes of a glass fiber coupling that allows for externally connecting a glass fiber for light intake without the need to open the box. During our campaign, the exposure times for individual spectra under clear-sky were around 15 ms. Typically, we coadded 30 spectra leading to effective exposures of several hundred ms.*

We add some text and a figure providing information on the telescope:



> *New Figure 3. Sketch of the telescope used to feed sunlight into the UV spectrometer. The telescope was mounted into the outer part of solar light beam collected by the solar tracker. A prism feeds sunlight into the telescope (0.5-inch tube diameter, ~120 mm tube length) which consists of a UV-filter (Hoya U330), a lens (focal length f=40 mm), and a circular aperture (800 μm diameter) aligned to the focus of the lens. A polytetrafluoroethylene (PTFE) diffuser plate illuminates the glass fiber (400 μm diameter) which then guides the sunlight into the UV spectrometer.*

> *Page 4:*
> *Figure 3 shows a sketch of the telescope assembly. A prism (10 mm sidelength) reflects the incoming sunlight into 0.5-inch lens tube mounted on a kinematic platform (not shown). The light beam first passes a UV-filter (Hoya U330) that shields unused parts of the solar spectrum, then a lens (focal length f=40 mm) focuses the beam on a 800 μm wide, circular aperture. Further downstream, a polytetrafluoroethylene (PTFE) diffuser plate illuminates a 400 μm glass fiber that takes the light into the spectrometer box via the fiber coupling. To support optical alignment, the length of the lens tube is adjustable, the prism can be rotated, and the attitude of the whole telescope can be controlled through the kinematic mount.*

<<- Nothing is mentioned about the plume heights during the days of the experiments. It would be useful to know for future studies considering that the sensitivity of the technique is strongly dependent on the true distance to the plume and thus the dilution effect.>>

Our technique delivers measurements of the total gas column between the observer and the sun. Thus, dilution in the vertical dimension should not affect the sensitivity of our technique (as long as the sun is roughly overhead) since the technique would still catch the volcanic surplus of molecules.

Dilution in the horizontal dimensions, however, does affect our sensitivity. We make note of this effect in the discussion and conclusion section where we argue that deploying the spectrometers closer to source would enhance our precision (page 10, line 24). Horizontal dilution depends on the prevailing wind patterns and thus, horizontal dilution also depends on the height of the plume. For the days reported here, the general observation was that there was no major buoyant rise of the plume out of the crater (as seen by visual inspection of the plume condensate) but that the plume remained roughly at the altitude level of the crater region (above 3,100 m) and that it dispersed horizontally. Our direct-sun observations provide some limited information on plume altitude which originates from observing the plume under various viewing angles. Preliminary analyses [Dinger, 2016] show that the plume was indeed located between 3,000 and 4,000 m altitude. While these investigations confirm our visual inspection, they are preliminary and thus, we would prefer not to include it in the manuscript.

<<- p5 l7. Why not use the background VCD-scaled profiles from the stationary FTS measurements instead of the a priori profiles?>>

The retrieval of scaling factors does not impose side-constraints i.e. the scaling factors for the gas profiles are determined in a least-squares sense. Therefore, using a different initial guess or a priori for these scaling factors does not affect the retrieval except for the number of required iterations. The latter could be minimized by choosing a better initial guess. Since our a priori scaling factors are reasonably close to the true ones, the effect on the number of iterations is negligible.

<<- p5 l9. By "lower tropospheric" part you mean one or several layers in your RT model? Please specify how the constraint is set.>>

We scaled 4 layers in the RT model between 3.2 and 4.9 km altitude. In general, we did multiple test runs including the use of a different retrieval algorithm, allowing for scaling larger parts of the tropospheric profile or even the entire profile. Differences between the test runs were minor compared to the detected volcanic signals.

> *Page 5, line 9:*
> *we only scaled the lower tropospheric part of the vertical profile and adopted the a priori for the upper tropospheric and stratospheric part.*
> *->*
> *we only scaled the lower tropospheric part of the vertical profile (four layers between 3.2 and 4.9 km altitude) and adopted the a priori for the rest*

<<- p6 l10. What about atmospheric pressure. Does small variations in the detected VCD's also vary with surface pressure?>>

Yes, variations in atmospheric pressure would have a similar effect as variations of observer altitude. Ratioing by the retrieved O_2 column (equation (1)) takes this effect into account as well. For our setup, however, the topographic variations are large compared to meteorological effects.

We change the manuscript

> *Page 6, line 10:*
> *co-vary with observer altitude*
> *->*
> *co-vary with surface pressure, for our setup mainly variable due to variable observer altitude,*

<<- Figs4&5. There are some intra-plume dXCO$_2$ values which fall in negative values with as much as 1 ppm, while the precision is reported to be considerably smaller (3.7x10^{18} molec/cm^2). This value should also be converted to delta XCO$_2$ (ppm) to have an idea.>>

We add the precision estimate in units of ppm:

> *Page 7, line 30:*

It amounts to 3.7×10^{18} molec/cm^2 suggesting that individual ΔCO_2 measurements exceed the precision estimate by a factor 5 to 6.
->
It amounts to 3.7×10^{18} molec/cm^2 for ΔCO_2 (0.20 ppm for ΔXCO_2) suggesting that individual measurements exceed the precision estimate by a factor 5 to 6.

Please note that we use the word "precision" referring to the random error component. Negative values such as in Figs. 4 and 5 are most likely due to systematic effects as suggested in the manuscript (page 8, line 32).

<<The authors argument later that the transition from CO_2-rich to CO_2- poor plume might be the reason for negative values, while the other gases remain elevated. But if HF is being used as proxy for intra-plume measurements, then this doesn't explain it. Maybe a dCO_2/SO_2 and dCO_2/HF time series for these critical phases could support the idea that strong plume composition variations are happening within the same morning.>>

Figs. 9 through 12 include information on the measurement time through the colored filling of the symbols. On Sep. 23, Fig. 9 shows that the early transect (blue symbols, green filling) yields relatively high CO_2 and high SO_2. The later transect (blue symbols, yellow filling) shows low CO_2 (even negative) and low SO_2. Likewise, Fig. 10 shows relatively high SO_2 and high HF for the early transect (blue symbols, green filling). For the later transect (blue symbols, yellow filling), however, HF remains high while SO_2 is low. Thus, we would argue that Figs. 9 through 12 support our statement on changing plume composition.

<<- p7 l14. The authors state that "An improved setup might benefit from operating the stationary FTS closer to the trajectory of the mobile observatory". The way it is explained, the grey points on the plots from the mobile instruments are used to produce the time-dependent background function (P). So, it is not clear to me what is meant by this. Is it the difference between the red line and the blue crosses that they want to minimize? What for if it is not used in the calculations?>>

Indeed, the measurements of the stationary FTS (blue crosses) are not used for any calculations. We included them in the plots to justify our assumption on a smoothly varying background concentration (fitted by a straight line to the "grey" background measurements of the mobile FTS).

Initially, we planned to use the stationary FTS measurements directly for background removal. Using the independent background measurements would have the advantage that we would not need to interpolate between background measurement before and after a plume transect. However, we refrained from doing so, since there is a small (so far unexplained) difference between the stationary FTS and the mobile background measurements. In the manuscript, we speculate that this difference might be due to the stationary and the mobile FTS observing different (background) air composition. Bringing the two instruments closer to each other would reduce this source of uncertainty.

<<- p10 l8. I don't see how wind direction could affect the observed variations. Should't the plume contain a mixture of all craters 5-10 km downwind?>>

Mt. Etna's crater region consists of four larger craters that are separated by several hundred meters in the horizontal (up to a kilometer between the North-East and the South-East crater) which is smaller than our sampling distance but not negligible. Further, the craters are somewhat displaced in the vertical and thus, they might be subject to different wind patterns. Voigt et al., 2014, also observed incomplete mixing of plumes at Mt. Etna (see in particular Fig. 1 in Voigt et al., 2014). Thus, wind direction can matter for plume observations at Mt. Etna. We add the reference to Voigt et al., 2014, at page 10, line 4.

<<- Figs6-8. There are clear intra-plume measurements of SO_2 and BrO which are not red-colored. Please include an explanation in the text why this is so, I couldn't find it.>>

We add the information in caption of Figure 6.

Fig. 6, caption:
Red closed symbols indicate intra-plume soundings where the UV-measured species SO_2 and BrO are averaged over the integration time of coincident FTS soundings.
->
Red closed symbols indicate intra-plume soundings used for further interpretation. For the UV-measured species SO_2 and BrO, we only consider those intra-plume soundings that occur within the integration time of a coincident FTS measurement. Therefore, some SO_2 and BrO measurements that are clearly intra-plume are not red colored.

<<- Fig9. the offset in the ordinate for the different days should be made clearer in the plot and not only in the caption. Maybe they can start labelling the y-axis at 0 each time where the dotted lines are drawn.>>

The dotted lines in Figs. 9-12 indicate the offsets graphically (in addition to the text in the caption). In our opinion, putting multiple 0 labels on the y-axis is rather confusing.

<<- It would be useful for certain readers, maybe geochemists or other researchers who want to compare their previos investigations, to include average ratios for the entire campaign in the bottom of table 3.>>

We include the average VCD-ratios in table 3 (table and caption changed).

However, those averages have to be considered with caution. The VCD-ratios reported in table 3 are highly variable. The origin of variability is not measurement noise that averages out but rather geophysical variability of the parameters that volcanologists, geochemists and other scientists are interested in. Thus, taking campaign-average values as basis for further interpretation is inadequate.

<<- At the end it was unclear to me the benefit of having a fast-scan solar tracker if only stationary data during the stop-and-go periods were utilised for calculating the ratios.>>

The main benefit of the fast solar tracker was that it enabled SO_2 measurements while driving (page 4, line 13). Thereby, the operator on the passenger seat was able to tell whether the mobile spectrometers sampled intra- or extra-plume air masses. Thus, the fast-scan solar tracker was of great help for operating stop-and-go patterns. This aspect might be considered scientifically marginal, logistically and technically it was a key enabling aspect.

Of course, we hoped for being able to also measure CO_2 while driving. Although we did not succeed in this aspect, we gained valuable insight in how to improve the tracker for future campaigns.

<<Minor
- The paragraph in section 2 is too long, break into at least two paragraphs.>>

Done.

<<- p3 l32 …in order to increase measurement frequency.>>

Added.

<<- p4 l10. Compared to applications which require stationary deployment, volcanic …>>

Compared to previous stationary and ship-borne applications …

<<- p4 l26. … due to unstable tracking of the sun (or clouds passing by ?!)>>

due to unstable tracking of the sun or thin clouds passing by.

<<- p4 l32 along the vertical, -> along the optical path, and derived the corresponding vertical-columnn-densities (VCDs).>>

We kept the text as it was. The algorithm retrieves VCDs. The sentence suggested by the reviewer implies a two-step procedure which is not how it works.

<<- p5 l19. Climatological profiles from a specific model? Please specify.>>

We add

> *Page 5, line 19:*
> *we used climatological profiles*
> *->*
> *we used climatological profiles taken from the recommendations of the Infrared Working Group (IRWG) of the Network for the Detection of Atmospheric Composition Change (NDACC) for the mid-latitudes.*

<<- p5 l29. were dark spectra measured and subtracted?>>

Yes. We add

… after subtraction of dark current and offset spectra.

<<- p5 l30. remove "such">>

Done.

Additional References:

Dinger S., Direct sunlight spectroscopy of volcanic plume composition in the downwind plume of Mt. Etna, Master thesis, Heidelberg University, Germany, 2016

Voigt, C., P. Jessberger, T. Jurkat, S. Kaufmann, R. Baumann, H. Schlager, N. Bobrowski, G. Giuffrida, and G. Salerno, Evolution of CO_2, SO_2, HCl, and HNO_3 in the volcanic plumes from Etna, Geophys. Res. Lett., 41, 2196–2203, doi:10.1002/2013GL058974, 2014